RECOVERY OF LIQUID FUELS FROM OIL BEARING SEED

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CERTIFICATE

This is to certify that the work in this report entitled **"Recovery of liquid fuels from oil bearing seed"** submitted by **Rahul Sinha (108CH032)** in partial fulfillment of the requirements of the prescribed curriculum for Bachelor of Technology in Chemical Engineering Session 2008-2012 in the Department of Chemical Engineering, National Institute of Technology Rourkela, is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge the matter embodied in the report is his bona fide work.

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NOMENCLATURE

TBO	Tree-borne oilseeds
CSW	Cherry seeds
CSS	Cherry seed shells
LTC	Low Temperature Conversion
EFB	Empty Fruit Bunches
TGA	Thermo-gravimetric Analysis
PID	Proportional-integral-derivative
ASTM	American Society for Testing and Materials
SEM	Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas Chromatography-Mass Spectrometry
GCV	Gross Calorific Value
HDPE	High Density Polyethylene
PPC	Physical Plant Cost
PEC	Equipment Purchase Cost
PCI	Plant Cost Index

ABSTRACT

Energy is the symbol for economic growth and human development. In a growing economy like India, energy is an essential building block of its development. The ever rising cost of fossil fuel has forced major world economies, which are also major importers of fossil fuel, to examine renewable and cheaper alternatives to fossil fuel to meet their energy demand. Renewable biomass is considered as an important energy resource all over the world and for an agriculture based economy like that of India, the future prospects of being able to convert widely available bio-mass materials into various forms of fuel is most attractive. Pyrolysis is one of the latest technologies which have the potential to provide valuable liquid and gaseous fuels from these biomass sources. Production of energy from renewable biomass resources would also reduce atmospheric CO_2 increase associated with fossil fuel use. The objective of this study is to evaluate the energy potential of a thermo-chemical conversion platform of oil bearing biomass crop linseed with an aim of studying the physical and chemical characteristics of the bio-oil produced and to determine its feasibility as a commercial fuel. Kinetic study of the pyrolysis reaction was also done.

Keywords: *Pyrolysis, Linseed, Bio-Fuels, Activation Energy, FT-IR, GC-MS*

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

Energy has become a symbol for economic growth and human development. In current scenario, where the consumption of fossil fuels, in both rural and urban sectors, have increased exponentially over the past decades and is expected to increases in the same manner for next couple of decades will lead to increase in not only its market price but also in the greenhouse gas emissions. Thus, a dire need to put a control over its consumption has been felt by environmentalists and economists as well which has forced major world economies, which are also major importers of fossil fuel, to examine renewable and cheaper alternatives to fossil fuel to meet their energy demand. In regards to this, a lot of research work is going on around the globe on various alternative sources of energy such as solar, wind, geothermal, hydrogen, nuclear, biofuel or biomass etc.

In a growing economy like India, energy is an essential building block of its development. India is the world's 6th largest consumer of energy. Seeing the present growth rate of 1-4% per annum, the demand of energy is estimated to grow by 8 times by the year 2030. Every year India is losing substantial amount of foreign exchanges through import of crude fossil fuel, which caters to about 70% of the country's requirement. Renewable biomass is considered as an important energy resource all over the world and for an agriculture based economy like that of India, the future prospects of being able to convert widely available bio-mass materials into various forms of fuel is most attractive.

1.1.Bio-fuel Scenario

Worldwide, oilseed crops occupy an area of 166.36 million hectares with a production of 295.6 million tonnes and productivity of 1777 kg/ha [1]. In India, area under oilseeds is 23.7 million hectares with a production of about 25 million tonnes and a productivity of just about one ton/hectare. The oilseed production in the country presently meets only 60-70% of its total edible oil requirements and the rest is met through imports[2].

India also has a potential of collecting 5 million tonnes of tree-borne oilseeds (TBO) of which only 0.1-1 million tonnes are being collected presently [3]. In addition to the existing potential of TBO, there is about 60 million hectares of wasteland of which 30 million hectares can be suitably utilized for growing plantations of bio-fuel plants like Jatropha etc. As per estimates of the International Energy Agency, farmers could supply the world with about 10% of

its gasoline by 2025. Edible oils are used as biodiesel in Europe, USA and other countries, whereas for countries like India which are already short of edible oils, use of non-edible oils only seems to be a suitable option. In countries like Brazil, USA and Canada where food gains like corn and wheat are being diverted for ethanol production, India cannot afford this option owing to limited area for food production to feed a population of about 1.1 billion. In such case, plants producing oil-bearing seeds acts as boon for bio-fuel production.

As the demand for bio-fuels is increasing, more emphasis is led on producing a cost–competitive liquid transportation bio-fuel. The major issues concerning the technology development challenges include the utilization of multiple feedstock and optimization of process parameters, exploitation of by–products generated during the conversion processes, environmental & social impacts and economic feasibility.

1.2.Biomass

Biomass is the most abundant, renewable unexplored source of energy. It is organic in nature, basically comprising cellulosic and hemi cellulosic matter found in the bio-degradable material from energy crops, agricultural and forest wastes, industrial, consumer and animal wastes. The energy stored in biomass is derived from the solar energy absorbed by plants during photosynthesis. Plants absorb CO_2 from its surrounding and convert it into biomass by photosynthesis. The energy stored in biomass is derived from the solar energy absorbed by plants during photosynthesis. Biomass life cycle (Figure 1) indicates a high potential of being a clean energy source as it doesn't add any extra CO_2 to the atmosphere.

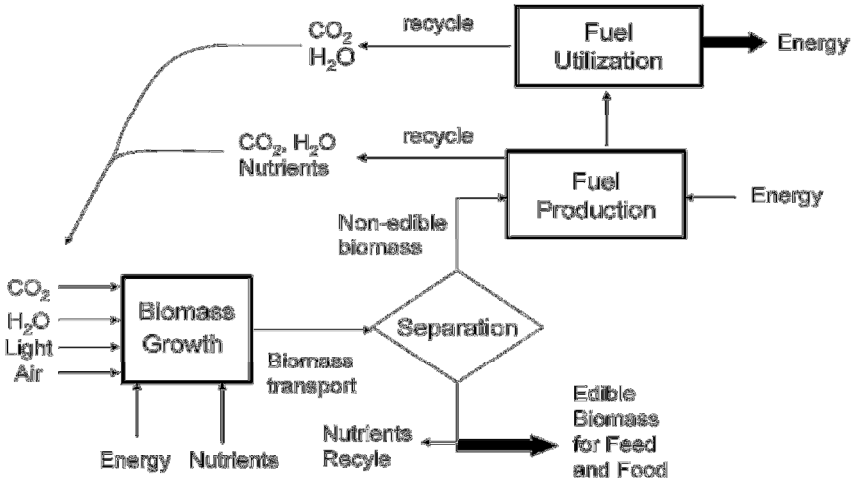

Figure 1: Biomass Life Cycle [4]

1.3. Bio-fuels

The energy rich compounds prepared from biomass are called bio-fuels. The bio-fuels obtained from different biomass are classified into solid, liquid and gases.

(a) Solid Bio-fuels

They are solid biomass that are combustible such as wood, compressed peat and dry bagasse etc., these can be burnt to get heat as a form of energy.

(b) Liquid Bio-fuels

This basically consists of liquid extracted from biomass and used as fuel and for production of other useful chemicals. This liquid stream consists of bio-oils and other organic chemicals mainly ethanol, methanol, acetone, acetic acid, bio-oils and bio-diesel (fatty acid methyl ester).

(c) Gaseous Bio-fuels

Gaseous product obtained from biomass decomposition contains primarily hydrogen, methane, carbon monoxide, carbon dioxide, ammonia and other gases dependingupon the organic nature of biomass and process condition.

1.4. Process for biomass conversion

There are basically three principal methods of biomass conversion which are shown in figure 2.

(a) Physical process

In this process the biomasses used are oil rich seeds. Oils are extracted from oilseeds and the extracted oil is refined by esterification with alcohol to reduce viscosity andimprove thequality of bio-fuels. This bio-fuel can be used as diesel substitute, so it isknown as bio-diesel.

(b) Biological Process

In biological processes, the wet biomass is used as raw materials. The wet biomass is treated with micro-organisms in the presence or absence of oxygen for a longer time. The mainproducts obtained in this process are bio-ethanol and biogas. Biological processes are of two types, fermentation and anaerobic digestion based on presence or absence of air.

(c) Thermo-chemical process

In these processes, the feed stock is heated in the presence (or absence) of oxygen or water for a short time. The products obtained are fuel gases and bio-oils which can be

upgraded by different other processes to get energy reach chemicals of various compositions. The different thermo-chemical processes are combustion, gasification, pyrolysis and hydrothermal liquefaction.

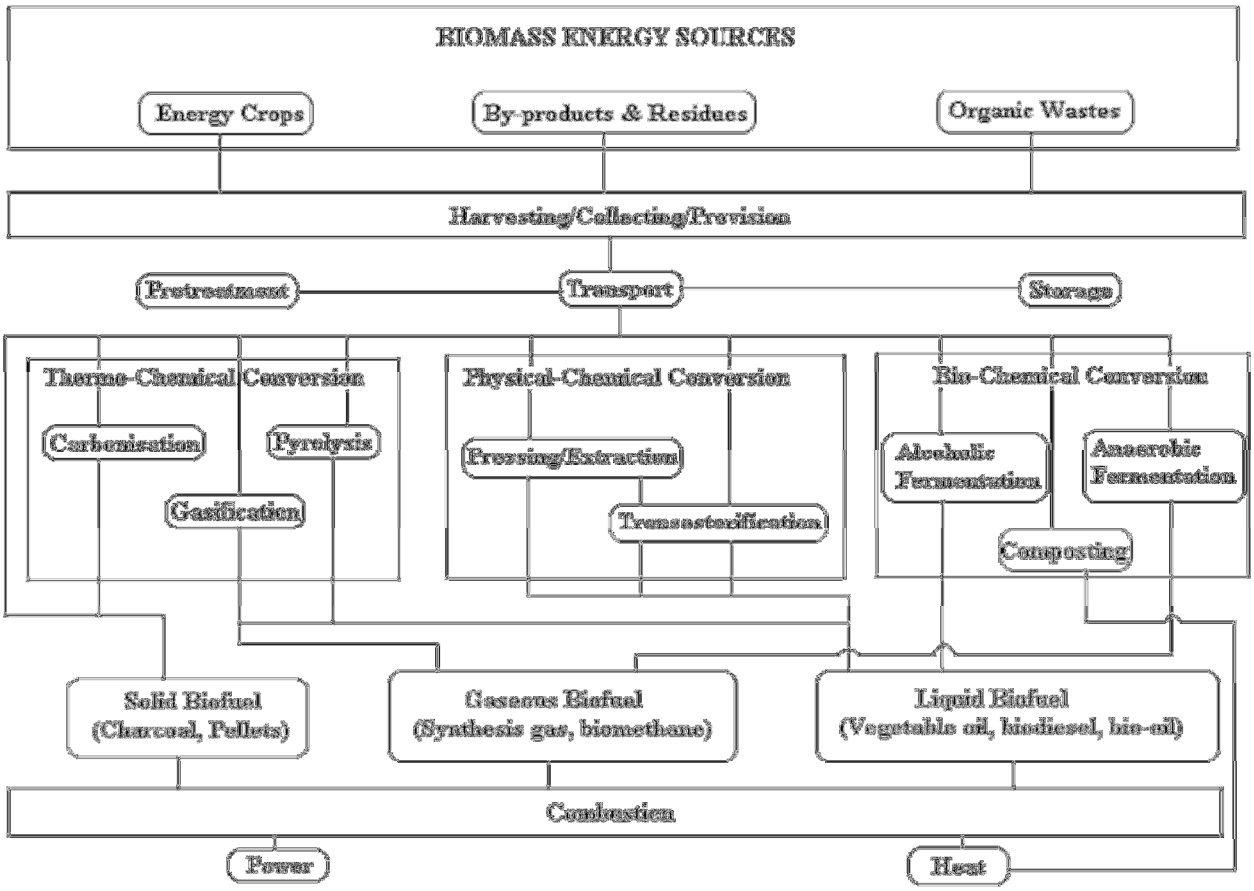

Figure 2: Principal methods of biomass conversion [5]

1.5. Pyrolysis

Pyrolysis is thermally initiated depolymerization process also known as thermolysis, which doesn't, involve any sort of oxidizing agent. Sometimes with limited supply of oxidizing agent and controlling the reaction leads to partial gasification. Pyrolysis product basically consists of gases like CH_4, CO_2, and NH_3 and liquids like ethanol, bio-oils, acetone, acetic acid etc. and solid as char. The relative proportion of the output depends upon the process and process condition, characteristics of biomass, optimum temperature and residence time of material. A brief flow sheet of the pyrolysis process has been shown in figure 3. The temperature controls the quantity of gas or liquid yield. A substantial change in the proportion of gas, liquid products and char is obtained with the change in rate of heating, temperature of the reaction and residence

time. In this process the biomass is heated to a temperature range with low residence time and rapidly cooled to collect the condensed liquid product. This is done to avoid the decomposition of the intermediate products during pyrolysis [6]. When cooled, most volatiles condense to from Bio-oil and remaining gases comprise a medium calorific value of non- condensable gases.

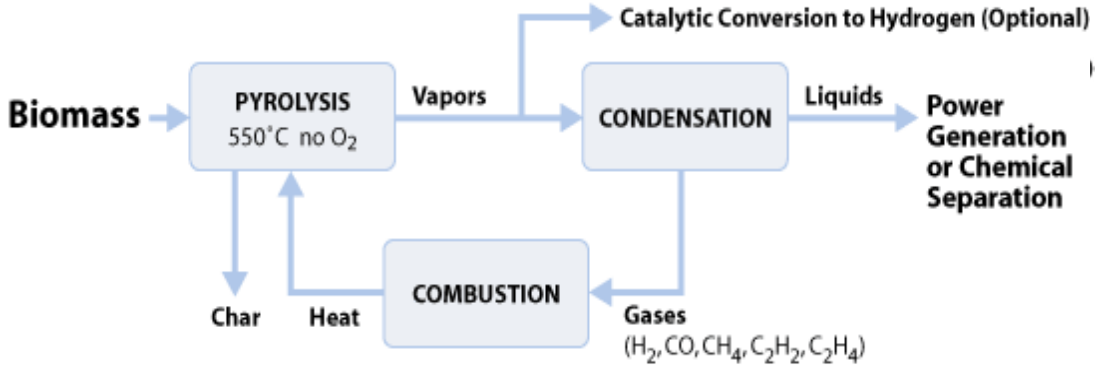

Figure 3: Pyrolysis process of biomass [6]

1.5.1. Comparison of different Pyrolysis Technologies

The residence time, heating rate, and temperature are the parameters that determine if thermo-chemical biomass treatments produce liquids, gases, or solids (Table 1). Process conditions that favor liquid products are short residence times, fast heating rates, and moderate temperatures. The liquids produced bypyrolysis are non-thermodynamically controlled products. Optimal residence times and temperatures are necessary to freeze the desired intermediates. Long residence times at lowtemperature produce primarily charcoal, and high temperatures produce mainly gas products [7].

Slow pyrolysis produces a large amount of coke, which can be used as a solid fuel, where as fast pyrolysis produces bio-oils in high yields of up to 80 wt% dry feed [8].

Table 1: Biomass Pyrolysis Technologies, Reaction Condition and Products [7]

name	residence time	temp (°C)	heating rate	major products
conventional carbonization	hours-days	300−500	very low	charcoal
pressurized carbonization	15 min-2 h	450	medium	charcoal
conventional pyrolysis	hours	400−600	low	charcoal, liquids, gases
conventional pyrolysis	5−30 min	700−900	medium	charcoal, gases
flash pyrolysis	0.1−2 s	400−650	high	liquids
flash pyrolysis	<1 s	650−900	high	liquids, gases
flash pyrolysis	<1 s	1000−3000	very high	gases
vacuum pyrolysis	2−30 s	350−450	medium	liquids
pressurized hydropyrolysis	<10 s	<500	high	liquids

[a] Adapted from Klass.[2]

1.5.2. Advantages of Pyrolytic oil

Pyrolysis is one of the most recent renewable energy processes, has been introduced and offers the advantages of a liquid product, bio-oil that can be readily stored and transported, and used as a fuel, an energy carrier and a source of chemicals. Bio-oils have been success fully tested in engines, turbines and boilers, and have been up graded to high quality hydro carbon fuels although at a presently unacceptable energetic and financial cost [9]. The production and the application of the bio-oil can take place at different locations and different moments in time. Pyrolytic oil can be storedfor long periods of time, and is therefore available when necessary.Transportation of pyrolysis oil is very convenient. Existing infrastructure can be used for transportation of pyrolytic oil. The pyrolytic oil produced from non-food related biomass is a second generation bio-fuel and therefore does not compete with the food industry. Pyrolytic oil can be used in applications where it substitutes for crude oil, doing so it offers a unique way to reduce dependency on fossil fuels. So many oil containing seeds are available in forest, can be collected by poor people which will be the revenuefor them. Just like fossil fuels, bio-fuels are burned in internal combustion,jet or even steam engines to provide power to move everything from pistons to turbines [10].

1.6. Alternative feed stocks for bio-fuel

A considerable amount of research has been done on alternative feed stocks. Table 2 lists estimated yields of traditional and alternative oil crops. Biofuels from many of these crops have been pysico-chemically tested and also some have been engine tested.

1.7. Pyrolysis of Biomass

Slow pyrolysis is also known asconventional pyrolysis. Conventional pyrolysis involves all three types of pyrolysis product(gas, liquid, and char). The slow pyrolysis of pomegranate seeds was carried out by Suat and Selhan at 400, 500, 600 and 800 °C to know the effect of temperature on the product distribution.The maximum liquid yields were obtained at the temperatures of500 and 600 °C and the bio-chars produced from pomegranate seeds having carbon rich fuels with high bulk densities and calorific values [12].

Fixed-bed slow and fast pyrolysis experiments have been conducted on a sample of rapeseed. The experiments were performed in two different pyrolysis reactors, namely a 3xed-bed Heinze and a well-swept 3xed-bed tubular retort to investigate the e2ects of heating rate, pyrolysis temperature, particle size, sweep gas velocity on the pyrolysis product yields and chemical compositions. The maximum oil yield of 51.7% was obtained in the Heinze reactor 550◦C, with a particle size range of +0:6–1:8 mm (sweep gas 100 cm^3 min^{-1} N_2) at a heating rate of 30◦C min^{-1} [13].

Table 2: Estimated yields of traditional and alternative oil crop [11]

Species	Common name and plant part	Oil yield (kg/ha)
H. brasiliensis	Rubber seed	50
C. viscosissima×*C. lanceolata*	Cuphea seed	120
K. virginica	Seashore mallow seed	100–153
C. tinctorius[1]	Safflower seed	200
S. indicum	Sesame seed	220
G. abyssinica	Niger seed	235
L. usitatissimum	Linseed	300
Gossypium hirsutum[1]	Cotton seed	340
T. catappa	Tropical almond nut	200–500
Glycine max[1]	Soybean	400
Arachis hypogaea[1]	Peanut	400
R. communis	Castor seed	450
Eruca sativa	Rocket seed	420–590
C. pepo	Pumpkin seed	540
Helianthus annuus[1]	Sunflower seed	580
Brassica rapa[1]	Rapeseed	600
P. tetragonolobus	Winged bean	350–900
C. cardunculus	Cardoon seed	500–750
Aleurites fordii	Tung nut	850
M. oleifera	Moringa seed	900
Coryllus avellana	Hazelnut	1000
S. glauca	Paradise tree seed	900–1200
B. carinata	Ethiopian mustard seed	900–1300
Cocos nucifera[1]	Coconut	900–1350
Pongamia (Milletia) pinnata/P. glabra	Koroch/karanja seed	225–2250
C. sativa	Camelina seed	1100–1400
T. peruviana	Yellow oleander seed	1575
B. aegyptiaca	Desert date kernel	1600
S. chinensis	Jojoba nut	1125–2250
J. curcas	Physic nut	1900–2500
A. indica	Neem seed	2670
I. polycarpa	Idesia seed	2250–3750
Elaeis guineensis (palm)[1]	Palm fruit	4300
C. esculentus	Yellow nut sedge tuber	4800–5500
C. inophyllum	Polanga seed	4680

Beis et al. studied the pyrolysis behavior of safflower seed in fixed-bed pyrolyzer to determine particularly the effects of pyrolysis temperature, heating rate, particle size andsweep gas flow rate on the pyrolysis product yields and theirchemical compositions and obtained the maximum oil yield of 44% at temperature of 500 °C, particle size range of +0.425–1.25 mm, with heating rate of 5°C/min and sweep gas (N_2) flowrate of 100 cm^3/min [14].

The effect of particle size on the yields of the pyrolysis products was investigated by Sensoz et al. on Brassica napus L. in a Heinze reactor under static atmosphere at a temperature of 500 °C at 40°C/min of heating rate with a particle size of rangeof 0.224–1.8 mm, maximum 46 wt.% oil obtained with a particlesize range of 0.85–1.8 mm with a heating value of 38.4 MJ/kg [15].

Rapeseed Pyrolysis were performed by Onay et al. in a free fallreactor at atmospheric pressure under nitrogen atmosphere toinvestigate the effect of final pyrolysis temperature, particle sizeand sweep gas flow rate on the yields of products and resulted thatthe maximum pyrolysis conversion of 78% at a temperature of 700 °C. The maximum bio-oil yield of 75% was obtained at a finalpyrolysis temperature of 600 °C, particle size range of 0.224–0.6 mm and the sweep gas flow rate of 100 cm^3/min [16].

Duman et al. studied the slow and fast pyrolysis of cherry seeds (CWS) and cherry seeds shells (CSS) in fixed-bedand fluidized bed reactors at different pyrolysis temperatures. The effects of reactor type and temperature on the yields and composition of products were investigated. In the case of fast pyrolysis, the maximum bio-oil yield was found to be about 44 wt% at pyrolysis temperature of 500 °C for both CWS and CSS, whereas the bio yields were of 21 and 15 wt% obtained at 500 °C from slow pyrolysis of CWS and CSS, respectively. Both temperature and reactor type affected the composition of bio-oils [17].

A Low Temperature Conversion (LTC) process carried out on a sample of castor seeds (Ricinuscommunis) by Figueiredo et al., generated fractions of pyrolysis oil, pyrolitic char, gas and aqueous extracts in the following relative amounts, respectively: 50%, 28%, 10% and 12% [w/w]. The pyrolysis oil was added at loadings of 2%, 5%, 10%, 20% and 30% [w/w] to commercial diesel. The density, viscosity, sulfur content, glow point, volatility and cetane index of these mixtures were determined. The results indicate that the addition of pyrolysis oil to commercial diesel results in fuel mixtures within the norms of ANP diesel directive no 15, made

on 19. 7. 2006, with the exception of the 20% mixture (which has an unfavorable viscosity) and the 30% mixture (which has an unfavorable viscosity and volatility) [18].

Pyrolysis behavior of cotton-seed cake was studied by Putun et al. under clinoptilolite catalyst at different conditions and investigated the effect of pyrolysis temperature, catalyst and sweeping gas flow rate and concluded that maximum 30.84% of liquid yield at temperature of 550 °C, sweeping gas flow rate of100 cm3/min in the presence of clinoptilolite catalyst (20% based on raw material) [19].

Putun et al. studied the rapid and slow pyrolysis of pistachio shell and concluded that the highest bio-oil yield with a value of 27.7% ata temperature of 773 K. when the heating rate and carrier gas flowrate were as 300 K/min and 100 cm3/min respectively [20].

Caoet al. studied the slow pyrolysis of waste corncob, observed a fasterrate of production at a temperature range of 350–400 °C and aslower at 400–600 °C whereas the yield of the liquid was nearly constant [21].

Zhongyang et al. investigated the pyrolysis behavior of different wood samples at temperature of 773 K in a fluidized bed reactor with a feed rate of 3 kg/h at atmospheric pressure and inert atmosphere and concluded that the higher ash content of biomass decreases the yield as well as the quality of bio oil [22].

Pyrolysis of Ellajjun oil shale was carried out by Omar et al.to know the effect of particle size on product components and observed that the yield of bio oil decreases with increase in particle size [23].

The pyrolysis of oil palm Empty Fruit Bunches (EFB) was investigated by Mohamad Azri et al. using quartz fluidized fixed-bed reactor. The effects of pyrolysis temperatures, particle sizes and heating rates on the yield of the products were investigated.The temperature of pyrolysis and heating rate were varied in the range 300–700 °C and 10–100 °C/min respectively. The particle size was varied in the range <90, 91–106, 107–125 and 126–250 lm. The result shows that the maximum bio-oil yield was42.28% obtained at 500 °C, with a heating rate of 100 °C/min and particle size of 91–106 lm [24].

Agrawalla et al. performed the thermal pyrolysis of groundnut de-oiled cake was in a semi-batch reactor at a temperature range of 200–500 °C and at a heating rate of 20 °C/min. The chemical analysis of the bio-fuel showed the presence of functional groups such asalkanes, alkenes, alkynes, aldehydes, ketones, carboxylic acids, esters, amines, nitriles, nitro

compoundsand aromatics rings. The physical properties of the bio-fuel obtained were close to that of diesel and petrol [25].

Goh Meng et al. investigated thepyrolysis behavior of oil palm shell in a fluidized bed reactor at temperature of 450 °C in presence of nitrogen gas and concluded that pyrolytic oil was rich in phenolic compounds [26].

Fluidized bed flash pyrolysis experiments have been conducted by Antony Raja on jatropha oil cake to determine particularly the effect of particlesize, nitrogen gas flow rate and temperature on the pyrolytic yield and obtained maximum liquid yield of 64.25% at temperatureof 500 °C with a particle size of 0.7–1.0 mm and at a nitrogen gasflow rate of 1.75 m^3/h [27].

1.8. Pyrolysis of Linseed

According to Indian Oilseeds and Produce Export Promotion Council [28], linseed production in India was 0.16 million tonnes in the year 2010-11.Linseed is a cool temperate annual herb with erect, slender stems, 60-80 cm tall. Traditionally, linseed has been grown for its oil, which is used in the manufacture of paints, varnishes and linoleum, because of its drying and hardening properties when exposed to the air and sunlight. Breeders have also produced linseed varieties that give oils with fatty acid profiles that make them suitable for culinary uses. This is because these “linola” types, containing a high proportion of linoleic acid and a low proportion of linolenic acid, have the appropriate stability and shelf life that the industrial types lack. The use of linseed oil has declined over the past several decades with the increased use of synthetic alkyd resins, which function similarly but resist yellowing [29]. It is edible oil but because of its strong flavor and odor, is only a minor constituent of human nutrition. In India linseed is widely used for cattle feed to provide nutritional supplements to animals. Thus, instead of wasting this oilseed it can be used as a vital source for biomass in a developing country like India. Irrespective of linseed being available easily, very little work has been carried out on it.

Linseed oil is a triglyceride, like other fats. Linseed oil is distinctive in terms of fatty acid constituents of the triglyceride, which contain an unusually large amount of α-linolenic acid, which has a distinctive reaction toward oxygen in air.

Typical % fatty acid content of industrial linseed oil:

C16:0 6% Palmitic
C18:0 2.5% Stearic Acid
C20 0.5% Arachidic acid
C18:1 19% Oleic acid
C18:2 24.1% Linoleic acid
C18:3 47.4% α-Linolenicacid
0.2% Other

Therefore, in this paper, pyrolytic oil is obtained by pyrolysis of linseed and has been characterized for its chemical and physical properties. Its properties were compared with those of commercial transportation fuels and other pyrolytic oils. Activation energy for the process is also determined using thermo-gravimetric analysis of the sample.

CHAPTER 2

MATERIALS & METHODS

2. MATERIALS AND METHODS

2.1. Raw material

The linseed and radish seed used in the experiment was bought from a fodder shop from a local market of Rourkela, Orissa, India.

2.2. Thermo-Gravimetric Analysis

As we know pyrolysis is heating of a substance in absence of air at a particular temperature, so, we need to determine the temperature for effective pyrolysis of the linseed. For this purpose, thermo-gravimetric analysis (TGA) of the sample seed was done using a DTG60 instrument in which round 20–30 mg of sample seed was taken and heated up to a final temperature of 700 °C with a residence time of 1 min at 700 °C. TGA was performed both in air and nitrogen atmospheres at a heating rate of 20 °C/min and one observation was taken at a heating rate of 25 °C/min. Thermo-gravimetric weight loss curve was plotted against temperature to find the range of temperature in which maximum thermal degradation of oil seed takes place.

2.3. Experimental procedure

The experiment was conducted in a reactor-furnace system in which the furnace temperature is maintained constant using a PID controller. The outlet of reactor was attached to a condenser to condense the vapors coming out of it and was collected in a collecting jar at the end of condenser. The seed sample was filled in a reactor of 300 ml and the reactor was kept in the furnace for heating at constant temperature. When the reaction starts, vapors coming out of reactor through the provided outlet are condensed in a condenser as shown in Fig. 4. Water is used as cooling medium in the condenser and circulated via a pump. The condensed vapors are collected in a container as the liquid product whereas there is some amount of non-condensable gases which aresimply left out. The liquid product collected contains oily water and bio-oil. Oily water is basically water with some dissolved hydrocarbons. Oily-water and bio-oil is further separated by difference in their density in a decanter.

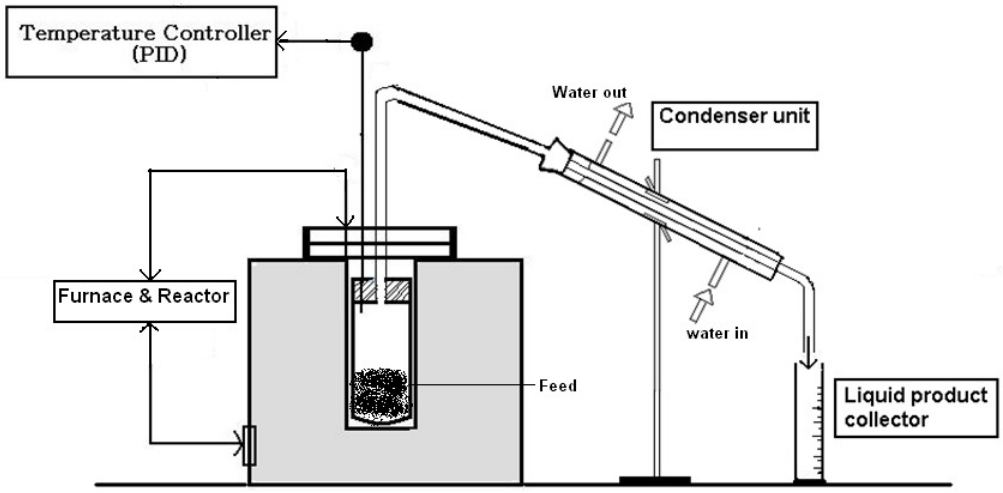

Figure 4: Experimental setup

2.4. Sample pyrolysis runs

Once the temperature range was established from the TGA curve then sample pyrolysis runs weredone with 30 gm of seed in that range at intervals of 50 °C to determine the temperature at which maximum yield ofliquid product is obtained. Various data like reaction time, yield of char, and yield of liquid product were noted down during sample runs. Variation in yield of char, liquid product and gas (volatiles) with respect to temperature is studied. Variation in reaction time with temperature was also plotted.

2.5. Characterization of raw material and char

Raw material (Linseed) and its char were analyzed to study the change in properties of the material due to pyrolysis and its effect on product.

2.5.1. Proximate analysis

It provides information on moisture content, ash content, volatile matter content and fixed carbon content of the material. It was carried out using *ASTM D3172-07a*[30]method.

2.5.2. Ultimate analysis

Ultimate analysis is performed to determine the elemental composition of the material. It was carried out using a CHNSO elemental analyzer (Variael CUBE Germany) which provides carbon, hydrogen, nitrogen, sulfur percentage composition. When sum of these components is

subtracted from 100, it gives oxygen percentage. Using the CHNS data empirical formula for the raw material is obtained.

2.5.3. Calorific value

Calorific value of a material is the amount of heat liberated when 1 kg of that material is burnt. It was determined for both seed and char using a bomb calorimeter (Model: AC-350, LECO Corporation, USA).

2.5.4. Oil content

Oil content of the raw material was found out using Soxhlet apparatus.

2.5.5. SEM of char

The surface of the char obtained was viewed under a Scanning Electron Microscope (Model: JEOL-JSM-6480LV SEM) at different magnification values to have a clear view on pore density and size.

2.6. Physical characterization of bio-oil

Physical properties such as density, specific gravity, viscosity, conradson carbon, flash point, fire point, pour point, cloud point,calorific value, sulfur content, distillation boiling range and cetaneindex of the bio-oil were determined using the standard methods given in table 3.

Table 3: Standard Methods for Physical Property Analysis

Physical Properties	Methods
Density	ASTM D1298 - 99
Kinematic Viscosity	ASTM D445 - 11
Conradson Carbon	ASTM D189 - 06(2010)e1
Flash Point	ASTM D6450 - 05(2010)
Fire Point	ASTM D1310 - 01(2007)
Pour Point	ASTM D5853 - 09
Calorific Value	ASTM D5468 - 02(2007)
Distillation Boiling Range	ASTM D2887 - 08

Cetane Index	ASTM D4737 - 10

2.7. Chemical characterization of bio-oil

2.7.1. FTIR

Fourier Transform Infrared Spectroscopy of the oil obtained after pyrolysis was done in a Perkin–Elmer Fourier transformed infrared spectrophotometer with resolution of 4 cmÿ1, in the range of 400–4000 cmÿ1 using Nujol mull as reference to know the functional group composition.

2.7.2. GC-MS

Gas chromatography–mass spectrometry of the pyrolytic oil is performed using a GC–MS-OP 2010[SHIMADZU] analyzer to determine the chemical compounds present in the oil.

GC Conditions:

Column Oven Temperature : 70˚C

Injector Temperature : 240˚C

Injection Mode : Split

Split Ratio : 10

Flow Control Mode : Linear Velocity

Column Flow : 1.51 ml/min

Carrier Gas : Helium 99.9995% purity

Injection volume : 1 microliter

Column Oven Temperature Program:

Rate	Temperature(˚C)	Hold Time(min)
-	70.0	3.0
10	300	9 [35.0 mts total]

Column:VF-5ms

Length:30.0m

Diameter:0.25mm

Film Thickness:0.25um

MS condition:

Ion source temp: 200 °C

Interface temp: 240°C

Scan range: 40 – 1000 m/z

Solvent cut time: 5mins

MS start time: 5(min)

MS end time: 35 (min)

Ionization: EI (-70ev)

Scan speed: 2000

CHAPTER 3

RESULT & DISCUSSION

3. RESULT AND DISCUSSION

3.1. Thermo-Gravimetric Analysis

The TGA curve (Figure 5) showed that the maximum thermal degradation of the linseedtook place in the temperature range of 250–550 °C in all the four. In this active pyrolytic zone, 76%weight loss was observed for linseed. In nitrogen medium, the high yield temperature range extended to 650 °C. However, the vapors obtainedduring this phase are generally higher hydrocarbons and are non-condensable. Thus temperature range of 550–650 °C was neglectedas it will not increase the yield of the required liquid product.The pyrolysis temperature range for most of the oil seeds liesin the temperature range of 400–800 °C.

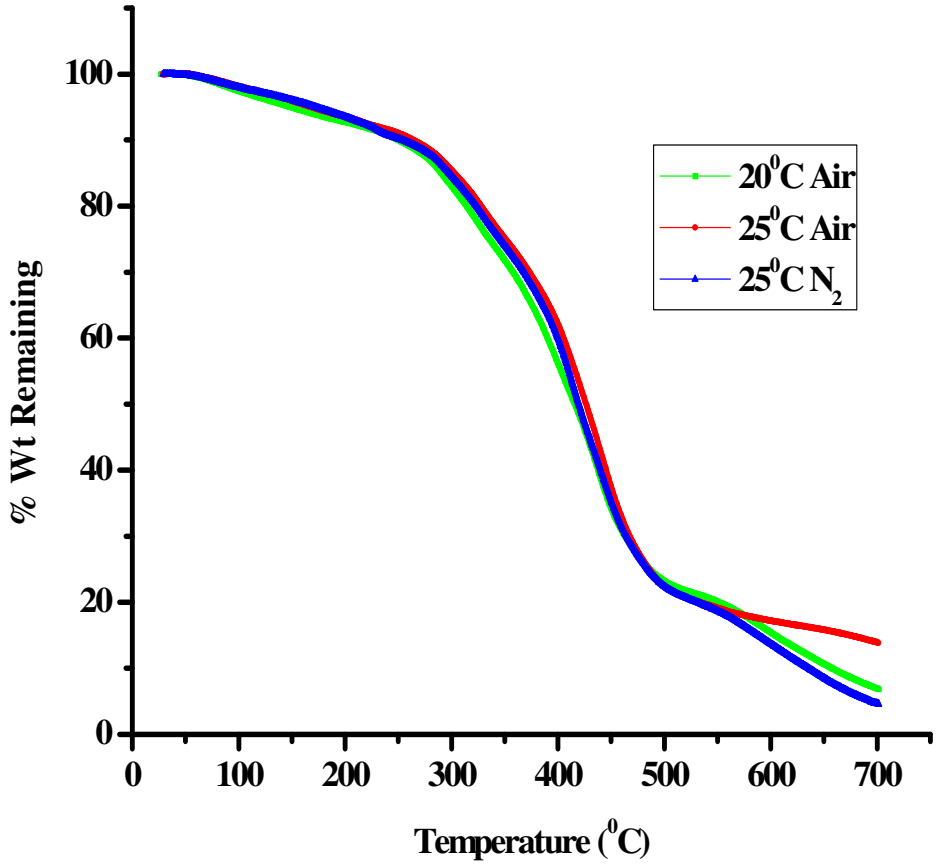

Figure 5: Thermo-gravimetric analysis of linseed

3.2. Sample Pyrolysis Runs

The plot (Figure 6) between yield of liquid, solid and gaseous products vs. temperature clearly shows that the yield of liquid product increases with increases in temperature up to 550°C and then it starts decreasing. Thus maximum yield of liquid product is obtained at 550°C which indicates it as effective pyrolysis temperature for linseed. Reaction time decreases with increase in temperature. Maximum yield of liquid product was around 68.26% obtained at the temperature of 550°C. The product distribution of linseed pyrolysis is shown in table 4.

Table 4: Distribution of different fractions at different temperatures in thermal pyrolysis of linseed

Temperature (^{0}C)	Oil (wt.%)	Gas/volatile (wt.%)	Residue (wt.%)	Reaction time in min.
350	11.17	24.67	64.16	90
400	30.67	16	53.33	50
450	33.7	30.83	35.47	37
500	50.87	26.8	22.33	26
525	60.93	18.24	20.83	22
550	68.26	10.54	21.2	20
575	45.97	33.4	20.63	19

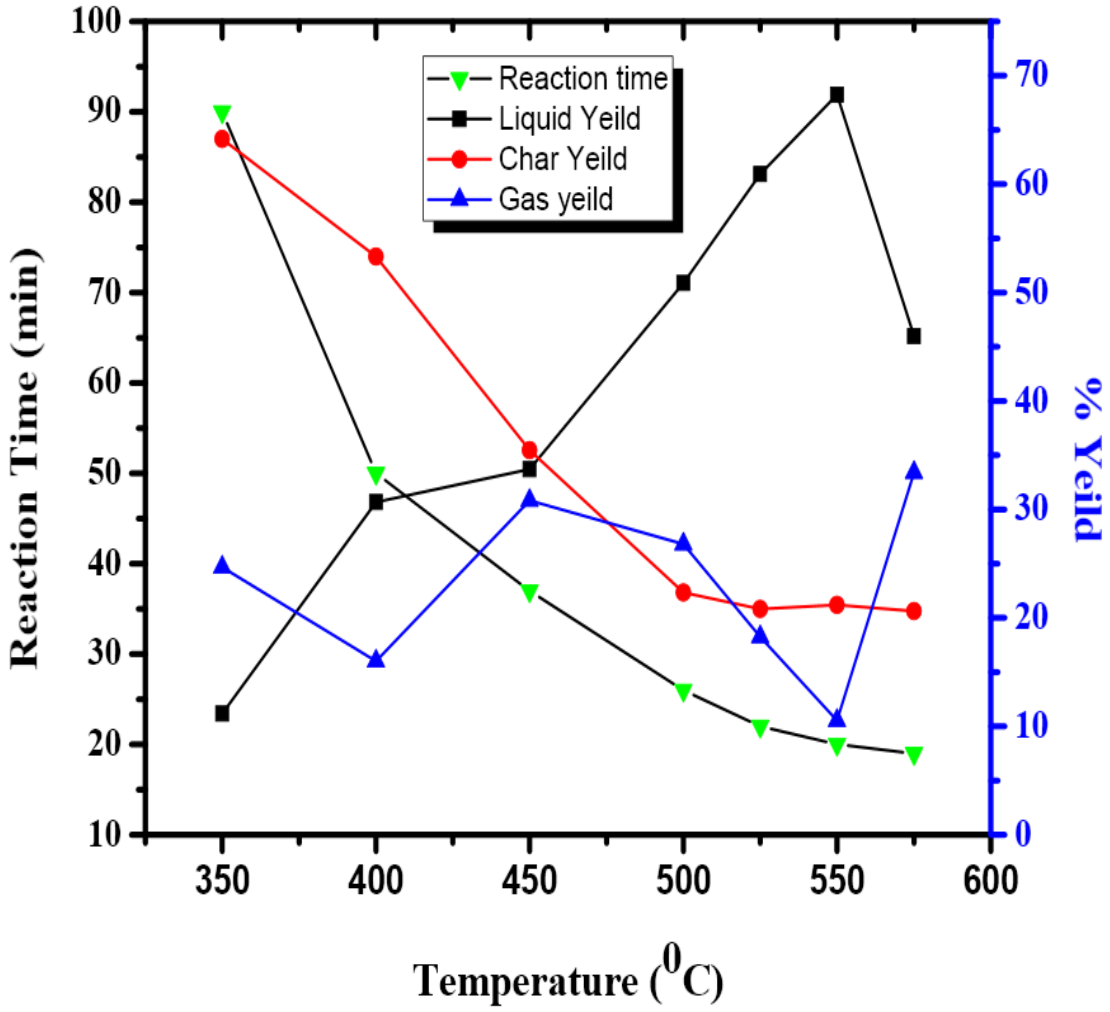

Figure 6: Yield vs. Temperature and Reaction time vs. temperature

3.3. Characterization of linseed and char

Proximate analysis of linseed and its char was done to determine the volatile matter, ash, fixed carbon and moisture content which is simplest way of investigating the fuel quality of solid materials. Low moisture and ash content in linseedshows that the biomass will have higher conversion efficiency and heating value and its energy quality will not deteriorate during storage as a result of decomposition. High volatile content indicates that the material is more volatile than solid fuels whereas loss in fixed carbon content during pyrolysis should be less. As it can be

observed in Table 5, linseed has a high volatile matter content of 85% which reduces to 23% after pyrolysis whichindicates the high yield of bio-oil will be obtained.

Ultimate analysis showed significant variation in carbon and oxygen content whereas there were slight variations in hydrogen, nitrogen and sulphur content.

Table 5: Characterization of linseed and char

	Linseed	Linseed Char
Moisture Content	6.9	0
Volatile Content	84.9	23
Ash Content	4.1	12
Fixed Carbon	4.1	65
C	64.986	69.351
H	9.942	4.804
N	3.583	5.136
S	0.227	0.048
O	21.262	20.661
C/H molar Ratio	0.54	2.05
C/N molar Ratio	21.23	15.76
% Oil Content	32.1	-
Empirical Formula	$C_{20.53}H_{36.52}O_{3.09}NS_{0.02}$	$C_{15.76}H_{7.66}O_{3.86}NS_{0.004}$
Gross Calorific Value(MJ/Kg)	24.06	33.74
Cellulose (%)	16.4	-

3.3.1. SEM Images

The images of the char surface obtained from scanning electron microscope (SEM) at magnification levels of 200 (Figure 7) and 1500 (Figure 8) clearly shows reasonable amount of pores present on the surface in 2-5 µm range.

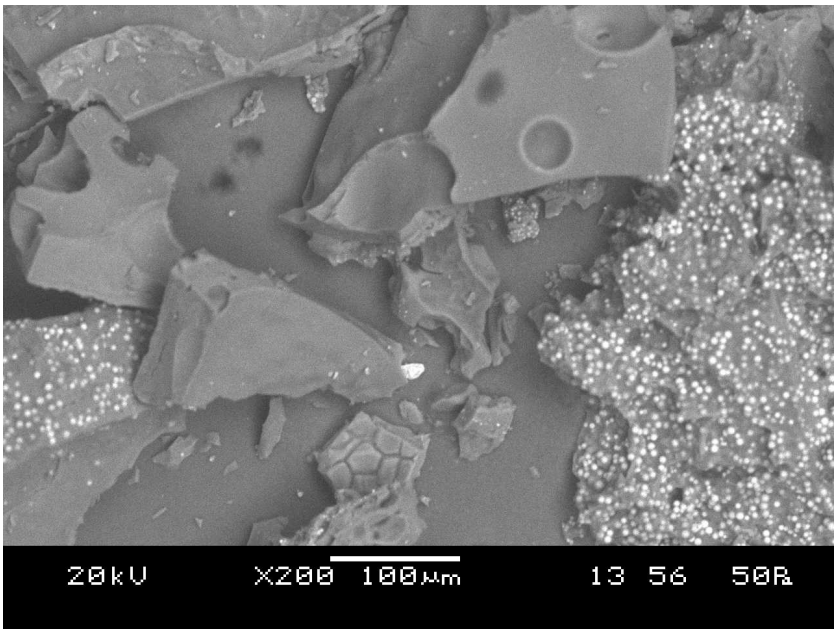

Figure 7: SEM image of Char surface at 200 magnifications

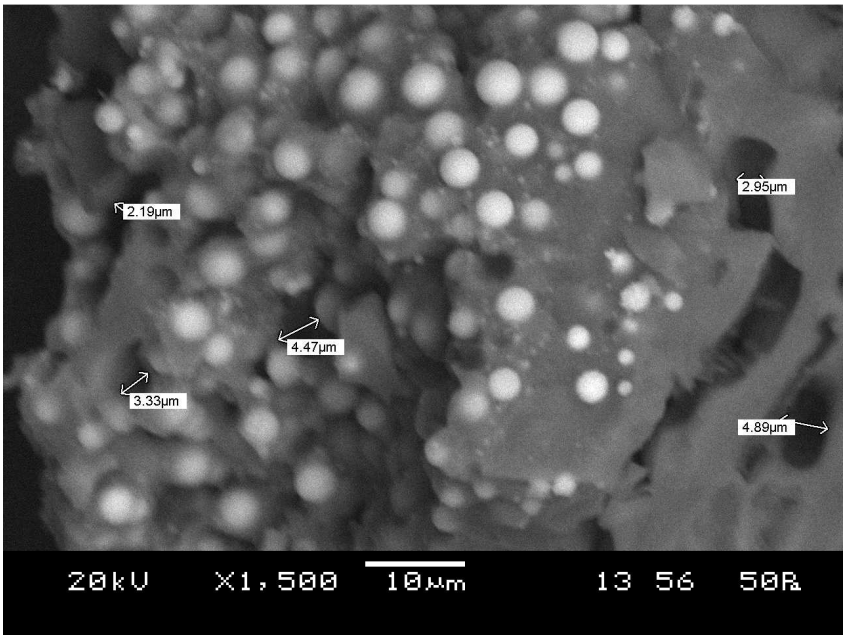

Figure 8: SEM image of Char surface at 1500 magnifications

3.4. Physical Properties of Bio-Oil

Physical properties such as density, specific gravity, kinematic viscosity, carbon residue, sulphur content, flash point, fire point, pour point, cloud point, gross calorific value, distillation

boiling range and cetane index of bio-oil which helps in assessing and determining feasibility of bio-oil as commercial liquid fuels is shown in Table 6.

Table 6: Physical Properties of Bio-Oil

Product Properties	Linseed Pyrolytic Oil
Density @ 15°C in gm/cc	0.9391
Specific gravity @ 15°C/15°C	0.9399
Kinematic viscosity @ 40°C in cst	1.97
Kinematic viscosity @ 100°C in cst	0.4
Pour point	3°C
Cloud point	15°C
Flash point by Abel method	24°C
Fire point by Abel method	32°C
Gross calorific Value in Kcal/Kg	8094
Sulphur Content	0.20%
Conradson Carbon Residue	1.94%
Calculated Cetane Index (CCI)	31
Distillation:	
Initial Boiling Point	90°C
Final Boiling Point	344°C

From comparison of physical properties of other pyrolytic oils and diesel and gasoline (table 7) it can be seen that linseed pyrolytic oil has higher density then transportation fuels like gasoline and diesel although viscosity is almost similar which may affect pumping and injection of fuel in the engine at lower temperatures. Density and viscosity of bio-oil can be modified by blending it with different transportation fuels and also by using various upgrading techniques. Flash point of bio-oil is in comparable range and hence will ensure safe storage but pour point is 3°C which will cause freezing problem in cold regions with sub-zero climate. Linseed bio-oil has good GCV of 34 MJ/Kg which is about 80% of that of gasoline and diesel. Thus, the GCV is good enough for a biomass based fuel although we will have somewhat less performance of engine. The distillation range showed that the bio-oil starts boiling at 90°C and the distillation

stops at around 344°C. It means the bio-oil contains substantial amount of volatiles as it initial boiling point is below 100°C. As it can be observed from Table, the properties of bio-oil were in similar range to that of other pyrolytic oils. From the comparison of carbon range it can be concluded oil obtained in this work lie between light and heavy petroleum products in this respect.

Table7: Comparison of Fuel Properties

Properties / Fuels	Specific Gravity 15°C/15°C	Kinematic Viscosity @40°C (cst)	Flash Point (°C)	Pour Point (°C)	GCV (MJ/Kg)	IBP (°C)	FBP (°C)	Chemical Formula
Linseed Pyrolytic Oil	0.9399	1.97	24	3	33.88	90	344	C_{10}-C_{23}
Gasoline[31]	0.72-0.78	-	-43	-40	42-46	27	225	C_4-C_{12}
Diesel[32]	0.82-0.85	2-5.5	53-80	-40 to -1	42-45	172	350	C_8-C_{25}
Bio-Diesel[32]	0.88	4-6	100-170	-3 to 19	37-40	315	350	C_{12}-C_{22}
Heavy Fuel Oil[33]	0.94-0.98	>200	90-180	-	- 40	-	-	-
Rapeseed Pyrolytic Oil[13],[16]	0.993	>40	62	6	36-37	-	-	$CH_{1.78}N_{0.04}O_{0.15}$
Safflower Pyrolytic Oil[14]	1.02-1.079	50-250	58-76	-16	38-41	92	315	$CH_{1.88}O_{0.15}N_{0.02}$

3.5. Chemical Composition of Bio-Oil

3.5.1. FTIR Analysis

FTIR analysis (Figure 99) suggests that the functional groups like alcohol, amines, phenyls, alkanes, alkenes, alkynes and nitro compounds may be present in bio-oil (Table 8). It is further confirmed with gas chromatography results.

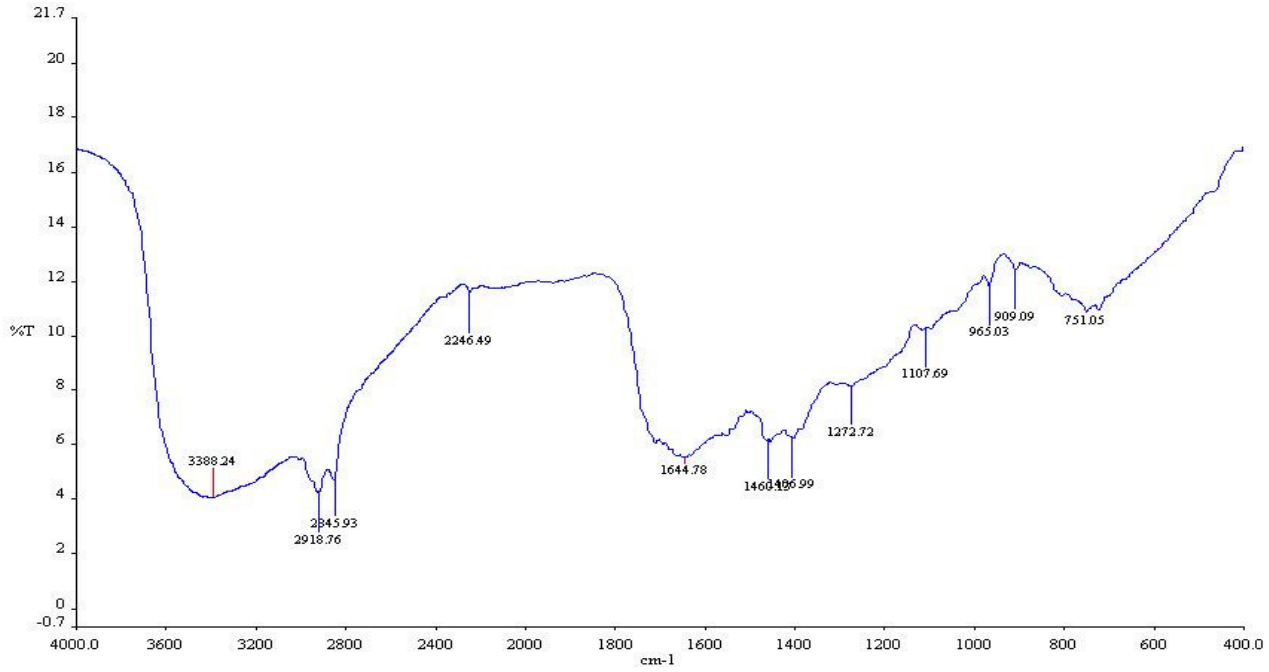

Figure 9: IR spectra of pyrolysis oil

Table8: FTIR Compound and frequency table

Compound Type	Frequency
O-H stretch hy bonded alcohol	3388.24
C-H stretch alkanes	2918.76
C-H stretch alkanes	2845.93
C≡C stretch alkynes	2246.49
NO_2asymmetrical stretching nitro compounds	1644.78
C-H scissoring and bending alkanes	1460.19
C-H scissoring and bending alkanes	1406.99
C-N stretch amines	1272.72
C-N stretch amines	1107.69
C-H bend alkenes	965.03
C-H bend alkenes	909.09
C-H bend phenyl ring substitution bands	751.05

3.5.2. Gas Chromatography-Mass Spectrometry

GC-MS analysis of the bio-oil was performed to find the chemical compounds present in it and to confirm the result of FTIR analysis. Various compounds present in the bio-oil were identified on comparison of the standard chromatogram data available with chromatogram obtained for the bio-oil. It was found that the bio-oil consisted of around 36 compounds as shown in table 9.

Table 9: Chemical Composition of Bio-Oil

Compound	Area %	Formula
6-dodecanone	1.37	$C_{12}H_{24}O$
Undecane	1.50	$C_{11}H_{24}$
1-undecanol	1.24	$C_{11}H_{24}O$
3-dodecene, (e)-	0.63	$C_{12}H_{24}$
Tetracyclo[3.3.1.0.1(3,9)]decan-10-one	1.74	$C_{10}H_{12}O$
Benzene, (1-methylbutyl)-	1.09	$C_{11}H_{16}$
2-Undecanone	1.24	$C_{11}H_{22}O$
Dodecane	2.01	$C_{12}H_{26}$
Benzene, hexyl-	1.09	$C_{12}H_{18}$
2-Methyl-4-phenylpentane	0.83	$C_{12}H_{18}$
1-Tridecene	1.71	$C_{13}H_{26}$
Tridecane	2.61	$C_{13}H_{28}$
1-Tetradecene	2.27	$C_{14}H_{28}$
n-Tetradecane	3.28	$C_{14}H_{30}$
1-Pentadecene	1.78	$C_{15}H_{30}$
Tetradecane	5.85	$C_{14}H_{30}$
1-hexadecene	2.31	$C_{16}H_{32}$
Heptadecane	3.42	$C_{17}H_{36}$
3-Heptadecene, (Z)-	4.56	$C_{17}H_{34}$
8-Heptadecene	5.06	$C_{17}H_{34}$
Hexahydroaplotaxene	1.09	$C_{17}H_{34}$

N-octadecane	6.35	$C_{18}H_{38}$
Benzene, (1-methyldecyl)	1.24	$C_{17}H_{28}$
Benzene, 1,1'-(1,1,3-trimethyl-1,3-propanediyl)bis-	0.84	$C_{18}H_{22}$
Heneicosane	1.15	$C_{21}H_{44}$
TRICOSANE	1.03	$C_{23}H_{48}$
2-TRIDECANONE	6.23	$C_{13}H_{26}O$
Tetradecanenitrile	2.22	$C_{14}H_{27}N$
Hexadecanoic acid, methyl ester	1.51	$C_{17}H_{34}O_2$
Oleanitrile	14.27	$C_{18}H_{33}N$
2-nonadecanone	5.75	$C_{19}H_{38}O$
Heptadecanenitrile	5.88	$C_{17}H_{33}N$
9-octadecenamide	3.15	$C_{18}H_{35}NO$
Oleic acid amide	1.11	$C_{18}H_{35}NO$
Stearamide	1.88	$C_{18}H_{37}NO$
N-Methyldodecanamide	0.71	$C_{13}H_{27}NO$

In chemical composition analysis, it has been observed that although the bio-oil contains around 70 compounds, it mainly consisted of 14.27% Oleanitrile, 6.35%n-octadecane, 6.23%2-tridecanone, 5.88% heptadecanenitrile, 5.85% tetradecane and 5.75% 2-nonadecanone accounting for around 45% of total mass. As it can be observed the bio-oil contains compounds with carbon chain length in the range of C_{10}-C_{23}which is similar to most of fuels used.

CHAPTER 4

KINETIC STUDY OF REACTION

4. KINETIC STUDY OF REACTION

Thermo gravimetric analysis (TGA) is one of the most commonly used methods to study the kinetics of thermal decomposition reactions [39]. Kinetic analysis of a reaction process gives information on the effect of various process parameters on the feedstock conversion. The raw material pyrolyzed here is linseed which belongs to biomass feedstock. It has been found by many researchers [34-38] that pyrolysis of biomass like linseed can be modeled like a cellulose pyrolysis. The pyrolysis cracking of cellulosic material can be modeled as 1st order reaction.

A (solids) → B (soilds) + C (volatiles)

For 1st order reaction, the rate equation is given by

$$\frac{dx}{dt} = k(1 - x)$$

Where,

$$k = ko * e^{\frac{-E}{RT}}$$

$$x = \frac{Wi - W}{Wi - Wf}$$

Hence,

$$\frac{dx}{dt} = ko * e^{\frac{-E}{RT}} * (1 - x)$$

Now considering heating rate β,

$$\frac{dx}{dt} = \frac{ko}{\beta} * e^{\frac{-E}{RT}} * (1 - x)$$

Now taking into account the effect of variation of temperature on conversion (x), the following equation represents the pyrolysis reaction:

$$\ln\left(-\ln(1 - x)\right) = \ln\left(\frac{KoRT^2}{\beta E}\right) - \left(\frac{E}{RT}\right)$$

Activation energy (E) is determined from the slope of the straight line plot (Figure 10) of ln(-(ln(1-x)) vs. 1/T using the TGA data.

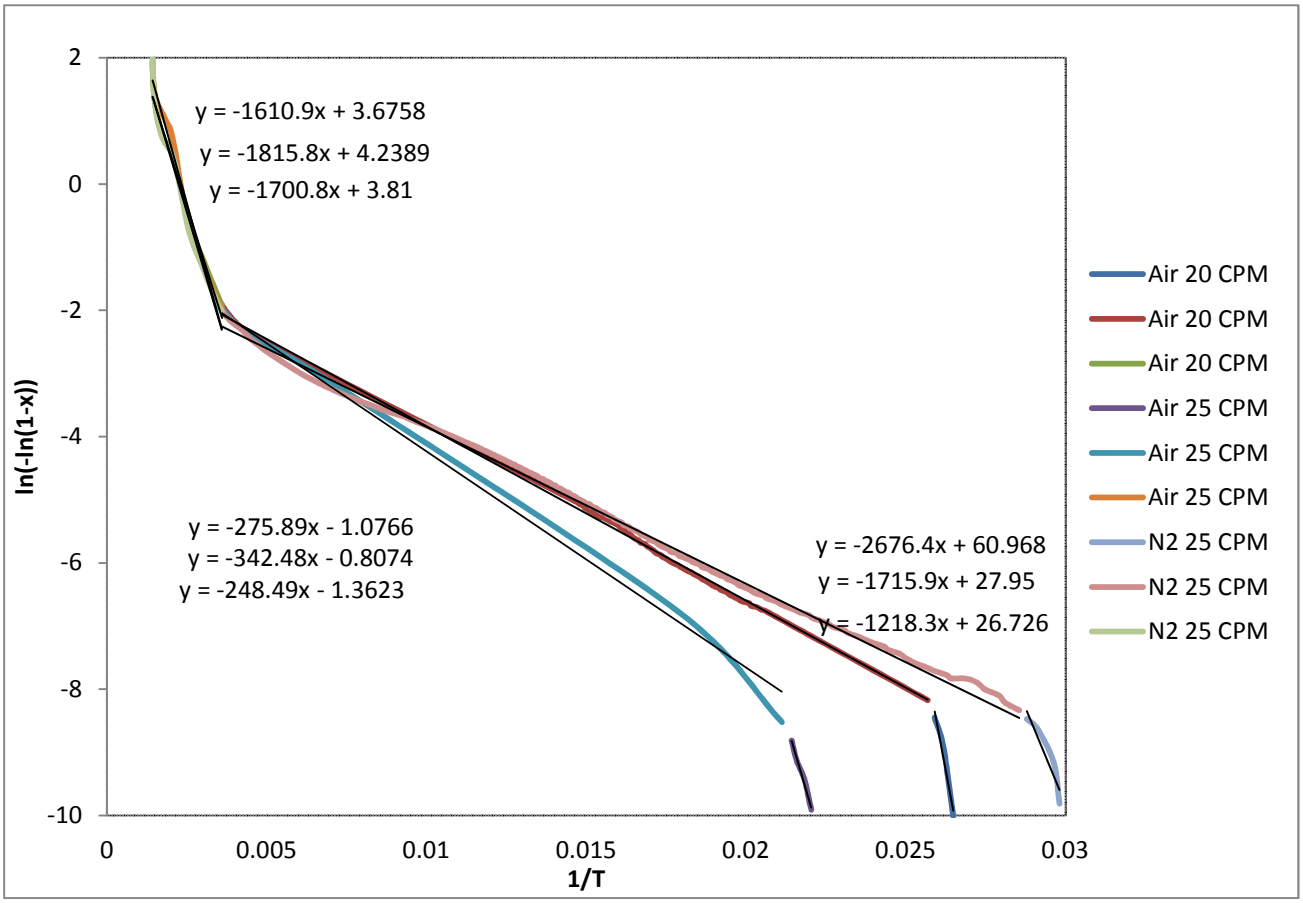

Figure 10: Kinetic analysis plot for determination of Activation Energy

Table10: Activation Energy for Pyrolysis of linseed

Sample	Activation Energy (KJ/Mol)		
	1st Phase	2nd Phase	3rd Phase
N2 25°C/min	10.1289462	2.06594586	14.1404512
Air 25°C/min	14.2659926	2.84737872	15.0965612
Air 20°C/min	22.2515896	2.29374946	13.3930226

The main aim of the kinetic study of pyrolysis reaction is to predict the activation energy for the reaction which shows the ease of occurrence of reaction. Reactions having less activation energy take place much easily than reaction with high activation energy. Thus, biomass having

less activation energy will be easily pyrolsed with lesser energy consumption. In this study pyrolysis of linseed has been performed at different heating rates and atmosphere to identify the best suited condition for its pyrolysis and corresponding activation energy (Table 10). Parekhet al. [36]has shown that pyrolysis of HDPE (High Density Polyethylene) have high activation energy as compared to that of pyrolysis of Jatropha (JC) and Karanja (KP). And when a mixture of HDPE and Jatropha is pyrolysed in 1:1 ratio, the activation energy for such reaction has decreased a lot. It means HDPE can be easily pyrolysed with 1:1 blend of Jatropha. Similar observation has been experienced for pyrolysis of HDPE and Karanja mixture in 1:1 ratio. Thus, biomass feed stocks having less activation energy for its pyrolysis reaction can be used as a blend to pyrolysis biomass feed stocks with higher activation energy. Activation energy for linseed pyrolysis is comparably low and hence can be used as a blend.

CHAPTER 5

INDUSTRIAL SCALE-UP & ECONOMIC ASSESSMENT

5. INDUSTRIAL SCALE-UP AND ECONOMIC ASSESSMENT

5.1. Aim

Design an industrial unit of capacity 12 tons/day for producing bio-oil by thermal pyrolysis of linseed.

5.2. Raw Material

Linseed (Linum usitatissimum)

5.3. Products

Table 11: Pyrolysis products and its uses

Product	Use
Linseed Pyrolytic Oil	Used as Bio-fuel.
Fuel Gas	Non-condensable vapors having high calorific value.
Char	Source of activated carbon. Also used as fuel.
Oily Water	Contains various useful hydrocarbons which can be extracted.

5.4. Process

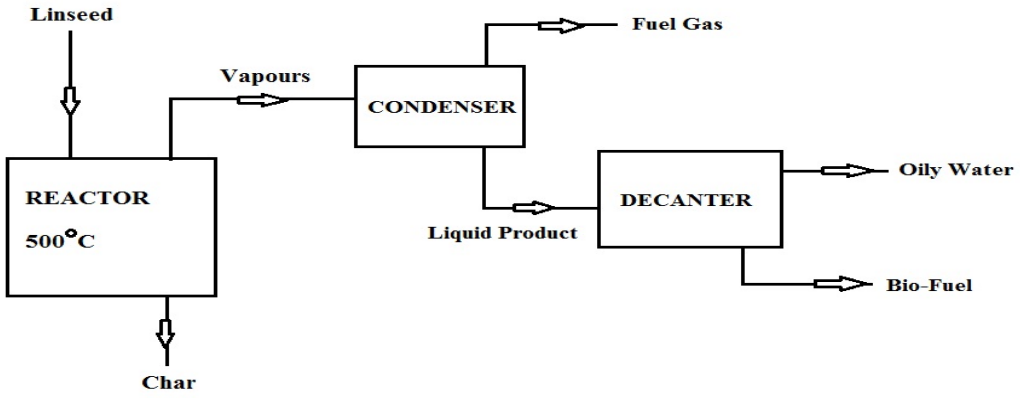

Figure 11: Process flow diagram of Pyrolysis unit

5.5. Material Balance

1 kg linseed produces ➡ 0.212 Kg Char

➡ 0.105 Kg Non-Condensable Vapors (Fuel Gas)

➡ 0.502 Kg Bio-Fuel

➡ 0.180 Kg Oily Water

Let us design the unit to process 12 tons of linseed in a single run.

12 tons of linseed produces ➡ 2544 Kg Char

➡ 1260 Kg Fuel Gas

➡ 6024 Kg Bio-Fuel

➡ 2160 Kg Oily Water

5.6. Energy Balance

5.6.1. Energy Balance for Reactor

Due to the complex nature of pyrolysis processes of biomass involving lots of simultaneous reactions, it is very difficult to keep an account of all processes while doing energy balance. Thus, for the sake of convenience, we measured the overall energy required for the pyrolysis of different amount of linseed by connecting an energy meter across the furnace (Table 12). A linear relationship was found out from the plot (Figure 12) of Mass vs. Energy consumed.

Table 12: Energy-Mass Analysis

Mass (gm)	Q (KJ)
30	2432
40	2460
50	2488
60	2516
70	2544

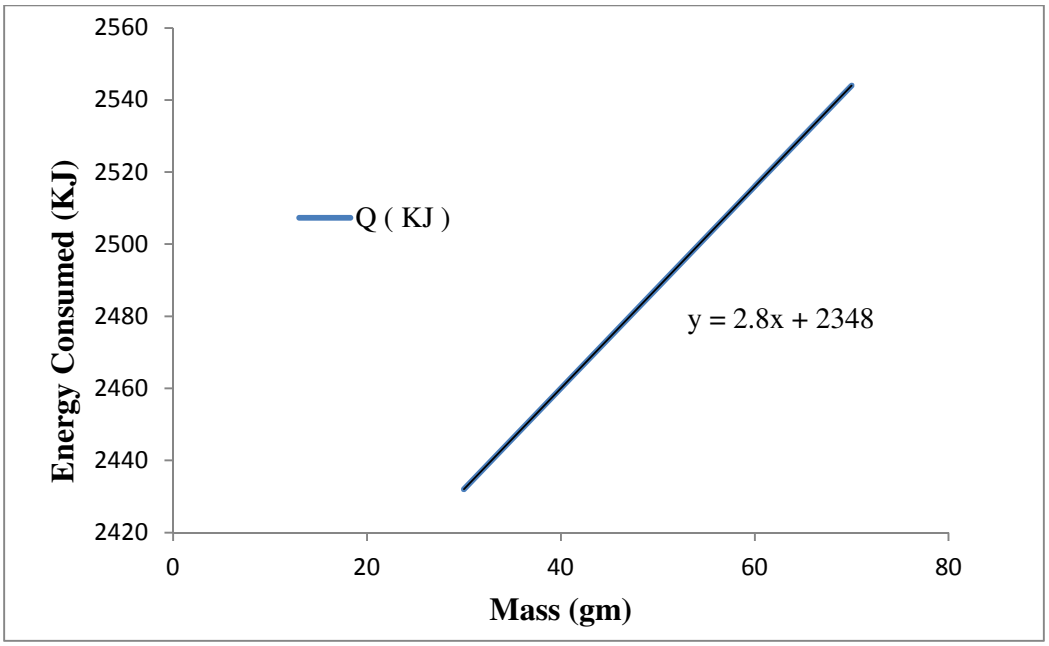

Figure 12: Mass-Energy consumption

Now using the linear relation, a rough estimation of energy required for pyrolysis of 12 tons of linseed was found out to be 33,600MJ. This energy is the amount of overall energy consumed by the process, i.e. energy to raise temperature of linseed from 35°C to 550°C along with energy consumed for pyrolysis reaction, whereas in industry the case will be different. Although the process is a semi-batch process but the furnace won't be allowed to cool down to room temperature after every run as it will cost a lot of energy loss. So, energy consumed is expected to be less than 33,600 MJ. Since it is a rough estimation, so calculation are done with 33,600 MJ only.

5.6.2. Energy balance for Condenser

As the operating temperature of the reactor and furnace system is 550°C so we assume temperature of the vapors coming out of the reactor to be at around 500°C.

Now,

(Vapors from Reactor) = (Fuel Gas) + (Bio-Fuel) + (Oily Water)

So, input for condenser = 9456 Kg of vapors which comprises of 1260 Kg of Non-condensable (Fuel Gas) and 8184 kg of condensable liquid product in which 6024 Kg is Bio-Fuel

and 2160 Kg is oily Water. Here also a very rough estimation has to be done in order to determine energy recovered while condensing. Here, the process is condensation of mixture of hydrocarbon vapors. In order to evaluate theenergy recovered during condensation and design the condenser mole fraction of each component of hydrocarbon vapor mixture is required with their specific heat capacity, thermal conductivity, viscosity, heat of vaporization, etc. which are not available. So, in this estimation,the hydrocarbon vapor mixture is considered as a single component hydrocarbon vapor with specific heat of vapor as 0.5 KJ/Kg K since it varies in the range of 0.5-3 KJ/Kg K for hydrocarbon vapors at constant pressure. Properties of oily water is also unknown and thus taken same as water, i.e. specific heat = 4.186 KJ/Kg K; latent heat of vaporization = 2300KJ/Kg at100°C.

It has been found in the literature that the specific heat of biomass pyrolysis oil lies in the range 2.5 KJ/Kg K – 3.5 KJ/Kg K [40].

We assume, Specific Heat = 2.61 KJ/Kg K.

Now, distillation range for bio-oil is given in Table 13.

Table 13: Distillation range for Bio-Oil

Initial Boiling point	90°C
Final Boiling Point	344°C

Now,

(Total Energy Recovered)=(Energy by Fuel Gas)+(Energy by Oily Water)+(Energy by Biofuel)

Energy by fuel gas = 1260*0.5*(500-40) = 2,89,800 KJ = 289.8 MJ

Energy by oily water = 2160*0.5*(500-40) + 2160*2300 + 2160*4.186*(100-40)

= 60,07,305.6 KJ = 6007.3 MJ

Energy by bio-fuel = 6024*0.5*(500-344) + 6024*2.61*(344-80)

= 46,20,648.96 KJ = 4620.6 MJ

Total Energy Recovered = (289.8 + 6007.3 + 4620.6) = 10917.7 MJ

Amount of cooling water @30°C required = 10917700/(4.186*40) = 65203 Kg = 65 tons

5.7. Equipment Size

5.7.1. Reactor

Cylindrical shape reactor made of carbon steel operating at 14.7 psi.

The reactor is assumed to work in a similar way to coke ovens used for coking of coal with a capacity of 12 tons processed at single run with a residence time of 20 hours.

Total Energy required for one run = 33,600 MJ = 31.84 M Btu

Time between two consecutive runs for discharging and loading = 1 hour

Total time for one run = 21 hours

Total no of runs per year = (365*24)/21 = 417 runs

Energy required per hour, Q = (31.84)/20 = 1.592 M Btu/hr

5.7.2. Condenser

1-4 Shell and tube exchanger with 21.25 inch shell inner diameter with a baffle spacing of 5 inch and 158 no of 16 inch long 13 BWG tubes with an outer diameter of 1 inch and a square pitch of 1.25 inch. Combineddirt factor of 0.003 should be provided.

Flow rate of vapors = (9456 Kg)/21 = 450.28 Kg/hr

Flow rate of cooling water = 65000/21 = 3095.23 Kg/hr

Inlet temperature of vapors = 500°C

Outlet temperature of vapors = 40°C

Inlet temperature of cooling water = 30°C

Outlet temperature of cooling water = 70°C

LMTD = 111.66°C R = 460/40 = 11.5 S = 40/(500-30) = 0.085 F_T = 0.8

$\Delta t = 0.8*111.66 = 89.35°C$

Shell Side (Cooling water):

Flow area = $(21.25*0.25*5)/(144*1.25) = 0.1475\ ft^2 = 137.03\ cm^2 = 0.014\ m^2$

Mass Velocity = $(3095.23)/(0.014)$ =2,21,087 Kg/hrm^2 =61.4132 Kg/m^2s

Equivalent diameter = 0.99/12 = 0.0825 ft = 0.025 m

Viscosity of water = $0.547*10^{-3}$ N s/m^2

Thermal conductivity of water = 0.6 W/m K

Reynolds number = $(0.025*61.4132)/(0.547*10^{-3}) = 2806.82$

$j_H = 28$

$h_o = 28*(0.6/0.025)*((4186*0.547*10^{-3})/0.6)^{(1/3)} = 1050.14\ W/m^2\ K$

Tube Side (Hot fluid):

Flow area = $(158*0.515)/(144*4) = 0.141\ ft^2 = 0.0131\ m^2$

Mass velocity = $450.28/(0.0131) = 34372.52$ Kg/hr $m^2 = 9.55\ Kg/m^2$ s

Viscosity of hydrocarbon vapor @240°C = $1.9*10^{-5}$ Kg/m s

Thermal conductivity of hydrocarbon vapor = 0.1385 W/m K

Reynolds number = $(0.021*9.55)/(1.9*10^{-5}) = 10555.26$

L/D = 16/0.0675 = 237

$j_H = 37$

$h_i = 37*(0.1385/0.021)*((500*1.9*10^{-5})/(0.1385))^{(1/3)} = 99.89\ W/m^2\ K$

$h_{io} = 99.89*0.81 = 80.911\ W/m^2\ K$

Clean overall coefficient, $U_C = (80.911*1050.14)/(80.911+1050.14) = 75.12\ W/m^2\ K$

Overall design coefficient:

Total Surface Area = 158*16*0.2618 = 662 ft^2 = 61.5 m^2

U_D= (10917.7 *10^6)/((21*3600)*(61.5*89.35)) = 26.28 W/m^2 K

Dirt Factor = (U_C - U_D)/(U_C*U_D) = (75.12-17.98)/(75.12*17.98) = 0.024 m^2K/W

5.7.3. Decanter

Input flow rate = 389.71 Kg/hr

Residence time = 18 Hrs

Volume of tank = 18*389.71 =7014.85 Kg liquid product = (1851.42/1000) + (5163.42/939.9)

= 1.85 + 5.49 = 7.34 m^3 = 1939.02gal

Volume of tank taken = 1900 gallons

5.8. Cost Analysis

Cost analysis provides a rough estimate of the total investment required to setup a plant of particular capacity, operating cost of the plant and production cost of the product. Cost analysis data will enable us to determine whether setting up such a plant is economically feasible and beneficial to society or not.

Total investment consists of two parts:

- Fixed Capital: - Total cost of plant ready for start-up.
- Working Capital: - Additional investment needed, over and above the fixed capital, to start the plant and operate it to the point when income is earned.

5.8.1. Factorial Method to Determine Total Investment:

$$C_f = f_l * C_e$$

Where,

C_f = Fixed Capital Cost

f_l = Lang Factor depending on type of process (Table 14)

Ce = Total delivered cost of all major equipment.

Basic Procedure:

• Prepare material & energy balance, preliminary flow sheets, size major equipment and select material of construction.

• Estimate purchase cost of major equipment using literatures.

• Calculate Fixed Capital using Table 15.

• Working Capital = 10-20 % of Fixed Capital.

• Total Investment = Fixed Capital + Working Capital.

Table 14: Lang Factors for Estimation of Fixed Capital [41]

Sl. No.	Item	Process Type		
		Fluids	**Fluids-Solids**	**Solids**
1	Major Equipment Purchase Cost (PCE)	1	1	1
f1	Equipment Erection	0.4	0.45	0.5
f2	Piping	0.7	0.45	0.2
f3	Instrumentation	0.2	0.15	0.1
f4	Electrical	0.1	0.1	0.1
f5	Buildings, Process	0.15	0.1	0.05
f6	Utilities	0.5	0.45	0.25
f7	Storage	0.15	0.2	0.25
f8	Site Development	0.05	0.05	0.05
f9	Ancillary Buildings	0.15	0.2	0.3
	Total Physical Plant Cost(PPC) = PCE*	3.4	3.15	2.8

	Total Physical Plant Cost (PPC)	1	1	1
f10	Design & Engineering	0.3	0.25	0.2
f11	Contractor's Fee	0.05	0.05	0.05
f12	Contingency	0.1	0.1	0.1
	Fixed Capital = PPC*	1.45	1.4	1.35

5.8.1.1. Major Equipment Costs

Reactor

Cost of cylindrical reactor made of carbon steel operating at 14.7 psi with an energy intake capacity (15 m^3) of 1.592MBtu/hr = $44,312 (2004 basis, PCI = 444).

Cost of reactor @2012 (PCI = 665) = (665/444)*45718 = $66,368

Condenser

A 1-4 fixed head shell and tube heat exchanger made of stainless steel with heating surface area of 61.5 m^2 and operating at pressure range of 10 psi is required.

Cost of exchanger @2004 = $52,000; Cost of exchanger @2012 = $77,882

Storage Tanks

Cost of Storage Tank 1 (acting as Decanter) of volume 10 m^3 @2004 = $11,545

Cost of Storage Tank 1 @2012 = $17,292

Cost of Storage Tank 2 of capacity 50 m^3 for storing bio-fuel (floating roof) @2004 = $37,404

Cost of Storage Tank 2 @2012 = $56,022

Cost of Storage Tank 3 of capacity 20m^3 for storing oily water @2004 = $14,482

Cost of Storage Tank 3 @2012 = $21,690

Thus major equipment purchase cost = reactor + condenser + 3 storage tanks

= $2,39,254 = Rs 1,19,62,700

5.8.1.2.Total Investment

Major Equipment Purchase Cost (PCE) = Rs 1,19,62,700

Total Physical Plant Cost (PPC) = 1.95*PCE= Rs 2,33,27,265

Fixed Cost = 1.35*PPC = Rs 3,14,91,807

Working Capital = 0.10*Fixed Cost = Rs 31,49,180

Total Investment = Fixed Capital + Working Capital = Rs 3,46,40,987

5.8.2. Operating Cost

It is the cost of producing the product and is needed to judge viability of project and to choose between alternate processes.

Annual Production Cost = A + B + C (From Table 7) (12)

$$\text{Production Cost (per Kg)} = \frac{Annual\ Production\ Cost}{Annual\ Production\ Rate} \quad (13)$$

Table 15: Operating Cost [41]

Sl. No.	Item	Typical Values
	Variable Costs	
1	Raw Materials	From Material Balance
2	Miscellaneous Materials	10% of item (5)
3	Utilities	From Flow Sheet
4	Shipping & Packaging	Usually Negligible
	Sub Total A =	1+2+3+4
	Fixed Costs	
5	Maintenance	5-10% of Fixed Capital
6	Operating Labors	From Manning Estimates
7	Laboratory Costs	20 – 23% of item (6)
8	Supervision	20% of item (6)

9	Plant Overheads	50% of item (6)
10	Capital Charges	10% of Fixed Capital
11	Insurance	1% of Fixed Capital
12	Local Taxes	2% of Fixed capital
13	Royalties	1% of Fixed Capital
	Sub Total B =	5+6+7+8+9+10+11+13
	Direct Production Costs =	A+B
14	Sales Expense	
15	General Overheads	
16	R&D	C= 20-30% of Direct Production Cost

Raw Materials

Cost of Raw Materials = 417*20*12000 = Rs 10,00,80,000

Miscellaneous Materials

Cost of Miscellaneous Materials = 0.10*0.05*3,14,91,807 = Rs 1,57,459

Utilities

Chilled Water @30°C = ((417*65*1)/100)*(665/444) = $406 = Rs 20,298

Electricity = {1.5*{(417*33,600) – (10917.7*417)}}/100

= $141877 = Rs 70,93,850

Cost of Utilities = Rs71,14,148

Maintenance

Cost of Maintenance = 0.05*3,14,91,807 = Rs 15,74,590

Operating Labors

Cost of Operating Labor = 20*3*500*365 = Rs 1,09,50,000

Laboratory Costs

Laboratory Costs = 0.2*1,09,50,000 = Rs 21,90,000

Supervision

Supervision Cost = 0.2*1,09,50,000= Rs21,90,000

Plant Overheads

Plant Overheads = 0.5*1,09,50,000 = Rs 54,75,000

Capital Charges

Capital Charges = 0.1*3,14,91,807 = Rs 31,49,180

Insurance

Insurance = 0.01*3,14,91,807 = Rs 3,14,918

Local Taxes

Local Taxes = 0.02*3,14,91,807= Rs 6,29,836

Royalties

Royalties = 0.01*3,14,91,807= Rs 3,14,918

Direct Production Costs = Variable Costs + Fixed Costs

= Rs 10,73,51,607 + Rs 2,67,88,442 = Rs 13,41,40,049

Sales Expense + General Overheads + R & D = 0.2*13,41,40,049= Rs 2,68,28,009

Annual Production Cost = 13,41,40,049+ 2,68,28,009 = Rs 16,09,68,058

Income from sales of Bio-Fuel = 417*6024*60 = Rs 150720480

Income from sales of Oily Water = 417*2160*45 = Rs 4,05,32,400

Income from sales of Fuel Gas = 417*1260*4.4767*1.32 = Rs 31,04,834

Income from sales of Charcoal = 417*2544*3*1.623 = Rs 51,93,911

Total Income from Sales = Rs 19,95,51,625

Net Profit = Rs 3,85,83,566

CHAPTER 6

CONCLUSION

6. CONCLUSION

- Maximum yield of 68.26% of liquid product is obtained by pyrolysis of linseed at 550°C.
- Linseed has high volatile matter content which is converted and collected as bio-oil.
- The bio-oil obtained shows comparable fuel properties and can be treated as moderate grade commercial fuels.
- In order to utilize it as commercial transportation fuel certain enhancement in properties like density, viscosity, corrosiveness and volatility have to be taken care off.
- The bio-oil contains nearly 36 chemical compounds of varying carbon chain length from C_{10}-C_{23} and functional groups such as alkanes, alkenes, alkynes, alcohols, ketones, aromatics rings, amides, nitriles and nitro compounds.
- Various valuable chemicals can also be extracted from bio-oil and oily water.
- Obtained char has a good calorific value, thus can be used as solid fuel and it can also be used as an adsorbent after further physical and chemical treatment.
- Activation energy of the pyrolysis of linseed was found out to be in lower range thus enabling it to be used as a blend for easy pyrolysis of materials with higher activation energy.
- Industrial scale-up and economic assessment was performed for the process but a lot of assumptions had to be taken to simplify the calculations and to take care of the insufficient data. The result of the economic assessment was satisfactory as it incurred a profit of 38 Millions INR annually based on plant of capacity 12 tons/day.

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